

Quantitative and Qualitative Prediction of Light Absorption by Colored Dissolved Organic Matter in the Coastal Zone

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LONG-TERM GOALS

To produce a physical water mass mixing model for describing colored dissolved organic matter (CDOM) distributions in the coastal zone. The model will combine the effects of local non-conservative processes with overall mixing of major CDOM end-members from terrigenous and marine sources. Although the model will be firstly derived for one study site (the entrance to the Baltic Sea) the approach will be designed for implementation in other regions of Navy interest (international estuaries and harbors).

OBJECTIVES

This project will provide a tool for predicting the quantitative and qualitative distributions of CDOM in the littoral zone based on combined model of CDOM biogeochemical cycling and physical oceanography. This approach provides the Navy with an alternative technique by which to gauge the performance of satellite based predictions of CDOM distributions. A major focus of this software will be the removal of CDOM “noise” in riverine and estuarine environments. My component of this project is to provide chemical analyses that validate or constrain the terrestrial and marine sources of the CDOM modeled by water mass.

APPROACH

The study area is the Baltic Sea-North Sea mixing zone at the entrance to the Baltic Sea (Figure 1). The Baltic Sea is a large estuary greatly influenced by freshwater inflow from its large drainage basin ($1.63 \times 10^6 \text{ km}^2$) and limited exchange with the North Sea (Atlantic Ocean). As a result its waters have a high content of terrestrially derived organic material.

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Figure 1. Map of the Baltic sea indicating the countries that border it. The red square indicates the proposed study site; the Baltic-North Sea mixing zone.

My component of this project supports the three work packages that will be produced from the project.

Work Package 1-Collection of a calibration data set

In order to achieve the goals of this project a comprehensive foundation of the seasonal variations in CDOM in these waters is needed. The concentrations and characteristics of CDOM in the freshwater run-off varies with season (Stedmon and Markager 2005). Additionally, in spring and summer there is production of CDOM associated with phytoplankton productivity in the surface waters, although the importance of this source relative to terrestrial CDOM is currently not known.

I am employing two methods to track the provenance of water masses and the source of CDOM in the Baltic-North Sea mixing zone. Method 1 is dual carbon stable isotope analyses of dissolved inorganic carbon (DIC) and DOC from water samples collected during each NERI cruise. I use a wet-chemical oxidation DOC analyzer coupled to an isotope-ratio mass spectrometer to make these measurements (Osburn and St-Jean, *in press*). Method 2 is the measurement of dissolved lignin concentration in selected surface and bottom water samples. Lignin is a ubiquitous tracer of terrestrial C, being synthesized only in vascular plants and is biologically recalcitrant. Dissolved lignin exhibits conservative behavior in most coastal environments and has been statistically related to CDOM absorption (Hernes and Benner 2003).

This work package will provide insight to the underlying chemical compositional variations in CDOM leading to changes in its absorption spectra. Basic oceanographic parameters (temperature and salinity) and other water quality data (e.g. Secchi depth, diffuse attenuation, nutrient concentrations, chlorophyll) will be provided by the Danish, Swedish and German monitoring programs.

Work Package 2- Model adaptation and validation (Responsible project partner: NERI).

The current hydrodynamic model being implemented for the Baltic-North Sea region at NERI in Denmark is COHERENS. My participation in this portion is limited.

Work Package 3- Integration (Responsible project partner: NERI).

The final phase of the project will involve the integration of the physical mixing model with our understanding of CDOM properties in these waters. Some initial studies suggest that despite the fact that DOM is a very dynamic component of several biogeochemical cycles, much of its variability in quantity and quality can be explained by conservative mixing (Højerslev et al 1996; Stedmon & Markager 2003; Hansel et al 2004). This is especially true for the months of the year outside of the phytoplankton growth season. During the spring bloom and summer bloom a significant amount of autochthonous CDOM is produced and adds to the background allochthonous signal. Recent work in Polish coastal waters has revealed that these deviations from conservative behavior can easily be modeled (accounted for) by including simple empirically derived models of biological production of CDOM (Kowalcuk et al 2006). A similar approach will be applied in this project. Firstly the properties of the CDOM end members in the mixing zone will be described and placed into the physical mixing model. Model prediction of CDOM distributions and characteristics will then be compared with measured values from WP1 and the degree of conservative mixing assessed. This will allow us to secondly evaluate the scale of impact of the non conservative processes (photochemistry and biological production) and hereafter include them when necessary using a multi-linear regression approach.

WORK COMPLETED

The project officially started in April 2006. Project planning meetings have been held at NERI in June 2006 and February 2007.

Work Package 1: To date six cruises have been completed and the samples from the first four are analyzed and the data is worked up. Each cruise consists of approximately 25 stations and 200 samples.

Work Package 2: Directed by NERI.

Work Package 3: Initial dissolved lignin measurements are underway. DIC measurements from four cruises are completed. DOC measurements on four cruises are near completion.

RESULTS

The initial combination of geochemical measurements is presented in Figure 2. The Arkona Sea represents the brackish Baltic Sea end member, having the largest DOC concentration with the strongest terrestrial signal in lignin concentration and stable isotope signature (-26.3‰; DOC stable isotopes are less negative for terrestrial sources. Marine DOC stable isotopes are between -19 to -22‰). September and October cruises are shown for the Kattegat stations. While surface waters were clearly more rich in lignin than were bottom waters, some seasonality was apparent. Note the larger concentration of dissolved lignin in Oct 06 for the Kattegat surface waters compared to Sep 06. Further, the $d_{13}C$ -DOC value for Kattegat surface water was more terrestrial than was Oct 06. At

depth, the bottom water source of the Kattegat station decreased in dissolved lignin concentration while the isotopic signature of the DOC showed more marine DOC influence (values became heavier).

Here it is clear that a large fraction of the variability in CDOM in these waters is explained by the mixing of the brackish Baltic Sea water rich in CDOM with the more saline North Sea water with lower CDOM concentrations. There appears to be two mixing gradients; a) across the salinity range of 8 to 31 representing the Baltic outflow and b) over the salinity range of 32-35 representing the mixing of a Baltic Sea/North Sea coastal intermediate water mass with offshore North Sea water. Initial analyses reveal that both mixing lines can be modeled reasonably well with linear models indicating that much of the CDOM in the region mixes conservatively.

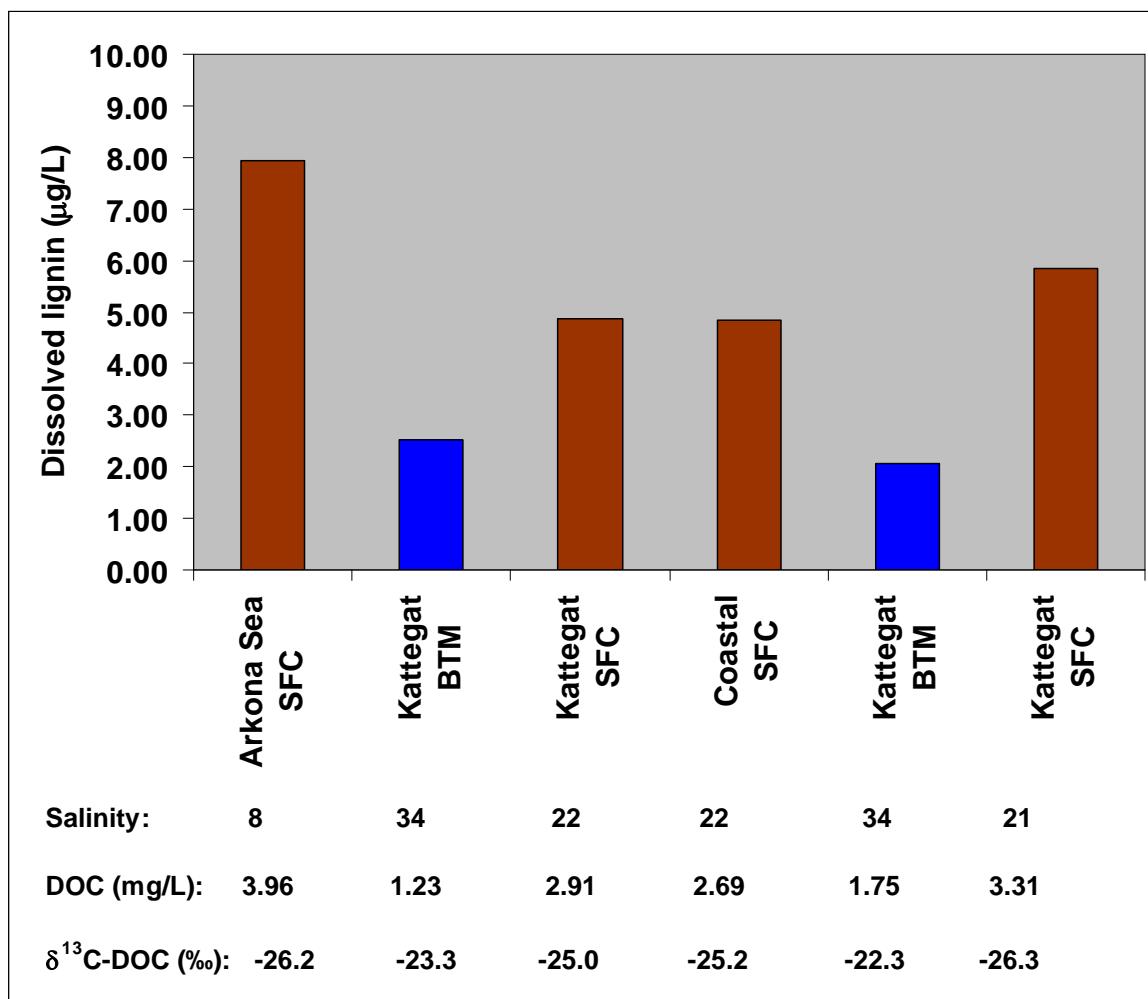


Figure 2. Geochemical measurements of CDOM in the North Sea-Baltic Sea mixing zone shows partitioning between water masses.

IMPACT/APPLICATIONS

The project area is relevant to the three major interest areas of the Ocean, Atmosphere and Space department (Code 32) at ONR: Battlespace Environments, Anti-Submarine Warfare and Mine Warfare. These three science and technology areas all have a vested interest in underwater optics in the coastal zone. The success of future development and increased application of airborne, satellite and submarine optical sensors in these waters is largely dependent on removing the CDOM signal. Dynamical physical mixing models are already used in a wide range of oceanographic research and monitoring applications, however the use of these for predicting CDOM distributions is not widespread. The proposed biophysical model would generate forecasting and nowcasting data to support the Navy's Littoral Remote Sensing program and FNC Littoral Antisubmarine Warfare as a major improvement in information awareness and characterization of the littoral battlespace, especially in terms of the inherent optical properties (IOPs) of water, or "water clarity." Data and/or forecasts of IOPs, for example, are useful to mission planners needing to predict diver visibility undersea in addition to the efficacy of laser- and camera-based detection systems under variable conditions in the littoral zone.

Finally this project will provide scientists with an improved understanding of CDOMs influence on the underwater light climate in these waters. Current ecological models do not take into account CDOMs effect on light attenuation and hence are not able to reproduce the correct photic depth, leading to elevated areal primary productivity estimates. With increased knowledge of the variability of CDOM and the integration of empirical models derived from this project a better estimation of the photic zone can be made in the models.

RELATED PROJECTS

There is a high degree of synergy between this project and another project held by C. Stedmon funded by the Danish Technical Science Research Council. The project is focused on improving fluorescence characterization methods for CDOM and providing increased insight on the correlations between its chemical and optical properties. Project started in 2005 and ends in 2007, with a budget of 1.4 million DKK (approx. US\$230,000).

REFERENCES

Hansel, D.A., Kadko, D. & Bates, N.R. (2004): Degradation of terrigenous dissolved organic carbon in the Western Arctic Ocean. *Science* 304: 858-861.

Højerslev, N.K, Holt, N. & Aarup, T. (1996): Optical measurements in the North Sea-Baltic Sea transition zone. I. On the origin of the deep water in the Kattegat. *Continental Shelf Research* 16: 1329-1342.

Kowalcuk, P., Stedmon, C.A., & Markager, S. (2006). Modeling absorption by CDOM in the Baltic Sea from season, salinity and chlorophyll. *Marine Chemistry* 101, 1-11.

Osburn, C. L. and St-Jean, G. (2007). The use of wet-chemical oxidation with high-amplification isotope ration mass spectrometry (WCO-IRMS) to measure stable isotope values of dissolved organic carbon in seawater. *Limnology and Oceanography: Methods*, 5, in press.

Osburn, C.L., Morris, D.P. Thorn, K.A. Moeller, R.E. (2001): Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation. *Biogeochemistry* 54: 251-278.

Stedmon C.A. & S. Markager (2005). Resolving the compositional changes in dissolved organic matter (DOM) in a temperate estuary and its catchment, using spectrofluorometry and PARAFAC analysis. *Limnology & Oceanography* 50(2): 686-697.

Stedmon, C., Markager, S & R. Bro. (2003): Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry* 82, 239-254.

Stedmon, C. & Markager, S. (2003): Behaviour of the optical properties of Coloured Dissolved Organic Matter (CDOM) under conservative mixing. *Estuarine Coastal and Shelf Science* 57, 973-979.

Stedmon, C.A., Markager, S. & Kaas, H. (2000): Optical Properties and Signatures of Chromophoric Dissolved Organic Matter (CDOM) in Danish Coastal Waters. *Estuarine, Coastal and Shelf Science* 51: 267-278.